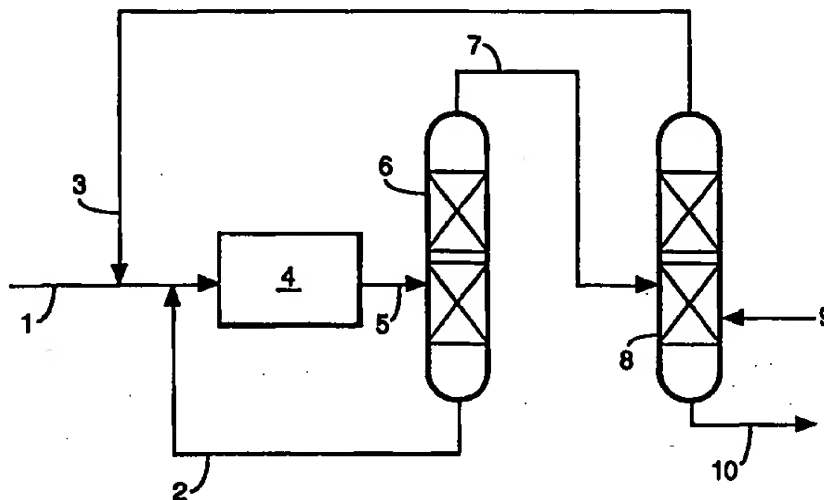




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 17/38, 19/08, 21/18, 17/386, 17/087		A1	(11) International Publication Number: WO 99/26907
			(43) International Publication Date: 3 June 1999 (03.06.99)
(21) International Application Number: PCT/GB98/03408 (22) International Filing Date: 12 November 1998 (12.11.98) (30) Priority Data: 9724831.4 25 November 1997 (25.11.97) GB 60/066,836 25 November 1997 (25.11.97) US (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): EWING, Paul, Nicholas [GB/GB]; 14 Alexandra Road, Stockton Heath, Warrington, Cheshire WA4 2UT (GB). (74) Agents: THOMAS, Ieuan et al.; Imperial Chemical Industries plc, ICI Group Intellectual Property, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).			(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: PREPARATION OF FLUORINE-CONTAINING ORGANIC COMPOUNDS



(57) Abstract

Preparation of a fluorine-containing organic compound by reacting a haloalkene with hydrogen fluoride wherein both the fluorine-containing organic compound and the haloalkene separately form azeotropes with hydrogen fluoride and wherein the haloalkene/hydrogen fluoride azeotrope is more volatile than the fluorine-containing organic compound/hydrogen fluoride azeotrope.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Preparation of Fluorine-containing Organic Compounds

The present invention relates to a process for the preparation of fluorine-containing organic compounds by reacting a haloalkene with hydrogen fluoride, particularly to a process for the preparation of hydrofluorocarbons from fluoroalkenes, more particularly to a process for the preparation of 1,1,1,2,3,3,3-heptafluoropropane from hexafluoropropene, azeotropes or azeotrope-like mixtures of a hydrofluorocarbon/hydrogen fluoride, particularly azeotropes or azeotrope-like mixtures of 1,1,1,2,3,3,3-heptafluoropropane/hydrogen fluoride and azeotropes or azeotrope-like mixtures of a haloalkene/hydrogen fluoride, particularly azeotropes or azeotrope-like mixtures of hexafluoropropene/hydrogen fluoride.

Hydrofluorocarbons are widely used as replacements for chlorofluorocarbon compounds in a variety of applications. Such applications include use in medical applications, for example as an aerosol propellant, use as a fire suppressant, use in refrigeration applications and in other applications. 1,1,1,2,3,3,3-heptafluoropropane, which is known in the art as Hydrofluorocarbon 227ea and will hereinafter be referred to as "HFC 227ea" for convenience, has zero ozone depletion potential and is particularly beneficial in medical applications in the light of its combination of properties including low toxicity, non-flammability, solvent properties and boiling point.

It is known to produce hydrofluorocarbons by the hydrofluorination of a fluoroalkene to the corresponding hydrofluoroalkane, optionally in the presence of a catalyst, in the liquid phase or vapour phase. Hydrogen fluoride is known for use as a hydrofluorination agent in such hydrofluorination processes.

A variety of materials may be employed as catalysts in such hydrofluorination processes.

For example, in the vapour phase reaction of fluoroalkenes with hydrogen fluoride for the preparation of hydrofluorocarbons, eg HFC 227ea from hexafluoropropene, DE 2712732 and GB 902590 disclose the use of a chromium oxyfluoride catalyst and an activated carbon catalyst respectively.

For example, in the liquid phase reaction of fluoroalkenes with hydrogen fluoride for the preparation of hydrofluorocarbons, eg HFC 227ea from hexafluoropropene, WO

97/11042 and WO 96/0243 disclose the use of catalysts comprising an organic amine complexed with hydrogen fluoride and certain antimony catalysts respectively.

The disclosures in the aforementioned patent specifications are incorporated herein by way of reference.

5 A stoichiometric excess of hydrogen fluoride to fluoroalkene is normally employed in the aforementioned processes and the degree of conversion of fluoroalkene to hydrofluorocarbon is dependent on *inter alia* the catalyst employed, if any, and the conditions in the reactor, etc.

The product from such reactions typically comprises the desired
10 fluorine-containing organic compound, organic by-products and hydrogen fluoride. For example, where the haloalkene is hexafluoropropene, which will hereinafter be referred to as "HFP" for convenience, the product stream leaving the reactor in which HFP is reacted with hydrogen fluoride typically contains HFC 227ea, HFP, hydrogen fluoride and azeotropes thereof.

15 It is normal practice to recover as much as possible of the hydrogen fluoride from the product stream from such hydrofluorination reactions for re-use. This may be partially achieved by distillation. However, the presence in the product stream of an azeotrope or azeotrope-like mixture of HFC 227ea/hydrogen fluoride and an azeotrope or azeotrope-like mixture of HFP/hydrogen fluoride limits the extent to which hydrogen
20 fluoride can be separated from the fluoro-organic compounds by simple distillation.

It is known that the stream comprising the hydrofluorocarbon/hydrogen fluoride azeotrope, eg HFC 227ea/hydrogen fluoride azeotrope, and the haloalkene/hydrogen fluoride azeotrope, eg HFP/hydrogen fluoride azeotrope, after recovery of a portion of the hydrogen fluoride by distillation, can be water-washed to allow recovery of both a
25 mixture of organic compounds essentially free of hydrogen fluoride and aqueous hydrogen fluoride. However, such a treatment is wasteful of hydrogen fluoride since it is normal practice for aqueous hydrogen fluoride generated in this way to be neutralised with caustic solution and/or lime and ultimately disposed of.

Alternatively, the product stream from the reaction of a haloalkene with
30 hydrogen fluoride, after recovery of a portion of the hydrogen fluoride by distillation, may be treated with a solution of alkali metal dissolved in anhydrous hydrogen fluoride

as described in our patent specification WO 97/13179. However, although such a process recovers hydrogen fluoride for re-use within the process, it has the disadvantage of requiring additional equipment.

Furthermore, it is known that in the preparation of fluorine-containing organic compounds by the reaction of a haloalkene with hydrogen fluoride the
5 haloalkene/hydrogen fluoride azeotrope can be separated from the fluorine-containing compound/hydrogen fluoride azeotrope by fractional distillation and hydrogen fluoride can be removed from the fluorine-containing organic compound/hydrogen fluoride azeotrope by treatment with water. However, treatment of the fluorine-containing
10 organic compound/hydrogen fluoride azeotrope with water to remove hydrogen fluoride therefrom involves the use of expensive equipment and is wasteful of hydrogen fluoride.

It will be appreciated that whereas aqueous scrubbing is an effective way of removing hydrogen fluoride from the organic compound(s) after reacting hydrogen fluoride with a haloalkene aqueous scrubbing tends to be expensive in terms of hydrogen
15 fluoride loss from the process. Preferably as much as possible, more preferably essentially all, of the hydrogen fluoride is separated from the product stream before aqueous scrubbing and particularly more preferably aqueous scrubbing is avoided.

Where in the preparation of a fluorine-containing organic compound by the reaction of a haloalkene with hydrogen fluoride the haloalkene/hydrogen fluoride
20 azeotrope is more volatile, ie has a lower boiling point, than the fluorine-containing organic compound/hydrogen fluoride azeotrope produced in the reaction we have now found that by (a) charging the reaction product to a distillation column, (b) introducing the haloalkene into the distillation column and (c) distilling the resulting mixture both the fluorine-containing organic compound substantially free of hydrogen fluoride and
25 the haloalkene/hydrogen fluoride azeotrope can be separated.

The separated haloalkene/hydrogen fluoride azeotrope can be recycled to the reaction vessel, can be used in another reaction or preferably at least a portion thereof is separated into a haloalkene-rich liquid phase and a hydrogen fluoride-rich liquid phase as is hereinafter more fully described.

30 According to the first aspect of the present invention there is provided a process for the preparation of a fluorine-containing organic compound by reacting a haloalkene

with hydrogen fluoride wherein both the fluorine-containing organic compound and the haloalkene separately form azeotropes with hydrogen fluoride and wherein the haloalkene/hydrogen fluoride azeotrope is more volatile than the fluorine-containing organic compound/hydrogen fluoride azeotrope characterised by the Steps of:

- 5 A. charging the haloalkene and the mixture comprising the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture, and optionally the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture, and/or hydrogen fluoride arising from the reaction of the haloalkene with hydrogen fluoride to a distillation column
- 10 B. recovering the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture, and the fluorine-containing organic compound from the distillation column separately; and
- C. optionally separating at least a portion of the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture, recovered from Step B into a
- 15 haloalkene-rich liquid phase and a hydrogen fluoride-rich liquid phase.

The reaction of haloalkene with hydrogen fluoride mentioned in Step A of the process according to the first aspect of the present invention may be carried out in the liquid phase or in the vapour phase, optionally in the presence of a suitable catalyst.

- Where Step C in the process according to the first aspect of the present invention
- 20 is carried out separation is typically effected by allowing the haloalkene-rich liquid phase and the hydrogen fluoride-rich liquid phase to separate under gravity.

- In a first embodiment of the process according to the first aspect of the present invention, the product of the reaction of the haloalkene with hydrogen fluoride is typically distilled to recover a portion of the hydrogen fluoride therefrom before the
- 25 mixture comprising fluorine-containing organic compound/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, haloalkene/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, and hydrogen fluoride is charged to the distillation column in Step A.

- The portion of hydrogen fluoride recovered by distillation prior to Step A, where
- 30 it is recovered, may be recycled to the reactor vessel.

In a second embodiment of the process according to the first aspect of the present invention, the product of the reaction of the haloalkene with hydrogen fluoride is charged directly to the distillation column in Step A.

Any hydrogen fluoride which is present in excess of that required to form azeotropes in the fluorine-containing organic compound recovered from Step B may be recovered, for example by distillation.

The haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, recovered from Step B may be fed directly to the reactor in which the fluorine-containing organic compound is produced or to an appropriate process stream(s) thereto containing the haloalkene, for example a stream containing the mixture of the haloalkene and hydrogen fluoride.

Likewise, where Step C is carried out, the hydrogen fluoride-rich phase and/or the haloalkene-rich phase recovered therefrom, may be fed directly to the reactor in which the fluorine-containing organic compound is produced or to an appropriate process stream(s) thereto containing the haloalkene, for example a stream containing the mixture of the haloalkene and hydrogen fluoride.

According to the second aspect of the present invention there is provided a process for the preparation of a fluorine-containing organic compound by reacting a haloalkene with hydrogen fluoride wherein both the fluorine-containing organic compound and the haloalkene separately form azeotropes with hydrogen fluoride and wherein the haloalkene/hydrogen fluoride azeotrope is more volatile than the fluorine-containing organic compound/hydrogen fluoride azeotrope which process comprises the steps of :

- A. charging a mixture comprising a haloalkene and hydrogen fluoride to a reactor; and
- B. optionally recovering at least a portion of hydrogen fluoride from the reaction products from Step A by distillation characterised by the further Steps of:
- C. charging the haloalkene and the mixture comprising the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, the haloalkene/hydrogen fluoride azeotrope, or

azeotrope-like mixture thereof, and HF from the reactor in Step A or, where Step B is carried out, the haloalkene and the mixture comprising the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, and the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, from Step B to a distillation column;

5 D. recovering a haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, from the distillation column in Step C;

E. recovering the fluorine-containing organic compound substantially free from hydrogen fluoride from the distillation column in Step C; and

10 F. optionally separating at least a portion of the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, recovered in Step D into a haloalkene-rich phase and a hydrogen fluoride-rich phase.

In the process according to the second aspect of the present invention, where Step F is carried out: the hydrogen fluoride-rich liquid phase can be recycled to a reaction vessel for the reaction of haloalkene with hydrogen fluoride or to a feed line thereto; and at least a portion of the haloalkene-rich liquid phase can be recycled to Step C.

In the process according to the second aspect of the present invention the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, recovered from the distillation column in Step D or the portion thereof not subjected to Step F, where Step F is carried out, may be recycled to the reaction vessel for the reaction of haloalkene and hydrogen fluoride or to a feed-line thereto.

According to a further aspect of the present invention there is provided an azeotrope, or azeotrope-like mixture, of HFC 227ea and hydrogen fluoride.

25 According to a yet further aspect of the present invention there is provided an azeotrope, or azeotrope-like mixture, of HFP and hydrogen fluoride.

Where HFC 227ea is prepared by reacting HFP with hydrogen fluoride in the process according to the second aspect of the present invention and where Step A is carried out in the liquid phase in the presence of a catalyst, eg TaF₅, NbF₅, or SbF₅, it is suitably carried out at a temperature in the range 20 to 200°C, preferably 40 to 120°C and especially 50 to 100°C. Suitably the reaction in Step A is carried out at

superatmospheric pressure such that the reactants are in the liquid phase for sufficient time to react to produce HFC 227ea. Preferably the pressure is at least 5 bar and more preferably the pressure is 10 to 50 bar.

5 The residence time in the reactor in Step A in the process according to the second aspect of the present invention is sufficient to permit conversion of haloalkene feedstock into fluorine-containing organic compound. The required residence time will be dependent on *inter alia* the degree of conversion required, the reactant ratio and the reaction conditions.

10 Haloalkene from Step F in the process according to the second aspect of the present invention is preferably recycled to the reactor in which the fluorine-containing organic compound is produced.

Where a low conversion rate of haloalkene into the fluorine-containing organic compound is desired it is preferable that the feedstocks be recycled to increase the yield of the fluorine-containing organic compound from the starting material. However, we
15 do not exclude the possibility that recycling is employed where high single pass conversions are required.

In Step A of the process according to the second aspect of the present invention the molar ratio of hydrogen fluoride (HF) to haloalkene fed to the reactor is suitably at least 1:1 and preferably 1.2 to 10:1. If a lower conversion rate is required a molar ratio
20 of HF to haloalkene of 0.1 up to 1:1 may be employed.

In Step A of the process according to the second aspect of the present invention the molar ratio of haloalkene to the catalyst is suitably not more than 100:1 and is preferably 1 to 50:1.

25 The levels of HF, haloalkene and catalyst in Step A of the process according to the second aspect of the present invention are suitably selected such that the catalyst and reactants remain dissolved in the liquid phase under the reaction conditions employed.

The process according to the second aspect of the invention may be operated in batch or continuous mode as desired. Semi-batch operation may also be employed in which one or more feedstocks are fed continuously to the process and one or more other
30 feedstocks are fed to the process in batch-wise fashion.

Alternatively, the process according to the second aspect of the present invention may be carried out in the vapour phase. Suitable conditions and catalysts for use in carrying out the process according to the second aspect of the present invention in the vapour phase are more fully described in DE 2712732 and GB 902590 mentioned
5 hereinbefore.

In Step C of the process according to the second aspect of the present invention and in Step A of the process according to the first aspect of the present invention the haloalkene and the mixture comprising fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, haloalkene/hydrogen fluoride
10 azeotrope, or azeotrope-like mixture thereof, are preferably simultaneously charged to the distillation column, and more preferably the haloalkene is charged to the distillation column at a point thereon below the point at which the mixture is charged thereto.

The process according to the first or second aspect of the present invention is applicable to mixtures of hydrogen fluoride with any haloalkene and any
15 fluorine-containing organic compound provided that the relative volatility of the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, is higher than that of the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof. Most hydrofluorocarbons, hydrochlorofluorocarbons and hydrofluoroethers form azeotropes or azeotrope-like mixtures, or azeotrope-like
20 mixtures, with hydrogen fluoride and the treatment of such mixtures is a preferred embodiment of the invention, especially the treatment of mixtures wherein the fluorine-containing organic compound is a hydrofluorocarbon, a hydrochlorofluorocarbon, a chlorofluorocarbon or a hydrofluoroether.

As examples of classes of fluorine-containing organic compounds which may be
25 prepared by the process according to the first aspect of the present invention may be mentioned *inter alia* hydrofluorocarbons (HFCs), eg pentafluoroethane and tetrafluoroethane, and hydrochloro-fluorocarbons (HCFCs), eg 1,1,1,2-tetrafluoro-2-chloroethane.

As examples of fluorine-containing organic compounds which may be prepared
30 by the process according to the first aspect of the present invention may be mentioned *inter alia* 1,1,1,2-tetrafluoroethane [HFC 134a], chloro-1,1,1-trifluoroethane [HCFC

133a], chlorotetrafluoroethane [HCFC 124/124a], pentafluoroethane [HFC 125], 1,1-difluoroethane [HFC 152a], 1,1,1-trifluoroethane [HFC 143a] and 1,1,1,3,3-pentafluoropropane [HFC 245fa].

Where the fluorine-containing organic compound prepared by the process according to the first aspect of the present invention is a hydrofluorocarbon, hydrochlorofluorocarbon or chlorofluorocarbon it will usually contain from 1 to 6 carbon atoms and preferably from 1 to 4 carbon atoms.

The present invention will be further illustrated by reference to the accompanying drawings which illustrate, by way of example only, schematic representations of plants for carrying out the process according to the present invention or temperature/composition plots for certain binary systems.

In the drawings:

Figures 1, 2, 3 and 4 are schematic representations of plants for carrying out the process according to the second aspect of the present invention in which Figure 1 illustrates the use of Steps A, B, C, D and E, Figure 2 illustrates the use of Steps A, B, C, D, E and F, Figure 3 illustrates the use of Steps A, C, D and E and Figure 4 illustrates the use of Steps A, C, D, E and F;

Figure 5 is a schematic representations of a plant for carrying out the second embodiment of the process according to the first aspect of the present invention; Figure 6 is a temperature/composition plot for the HFC 227ea/HF binary; and Figure 7 is a temperature/composition plot for the HFP/HF binary.

Although the processes according to the first and second aspects of the present invention are applicable to any of the aforementioned organic compounds they will be described hereinafter by reference to the preparation of HFC 227ea.

In Figures 1 and 2, feed pipe (1) leads to a reactor (4), which optionally contains a fluorination catalyst. Product pipe (5) from the reactor (4) is in fluid-flow communication with a first distillation column (6), which is for example a single stage flash vessel. Distillation column (6) is typically operated at a pressure of 12 bars with a bottoms temperature of 70°C and a tops temperature of around 50°C. Bottoms pipe (2) from distillation column (6) is in fluid-flow communication with feed-pipe (1). Tops line (7) from distillation column (6) is in fluid-flow communication with a second distillation

column (8), which is for example a packed column. Distillation column (8) is typically operated at a pressure of around 12 bars with a tops temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (8) is provided with a feed line (9) below the point at which tops line (7) is attached to it, a bottoms pipe (10) and a tops pipe (3) which is in fluid-flow communication with feed-pipe (1).

In Figure 2, tops pipe (3) from distillation column (8) is provided with a line (11) which is in fluid flow communication with phase separator (12). Phase separator (12) is provided with a line (13) in fluid-flow communication with feed line (9) and a line (14) in fluid-flow communication with tops line (3).

In operation, the reactor (4) is charged through feed pipe (1) with a feed stream containing fresh hydrogen fluoride, recycled hydrogen fluoride (from bottoms line (2) and tops line (3)) and HFP/hydrogen fluoride azeotrope (from tops line (3)). The product from reactor (4) (HFC 227ea, hydrogen fluoride and optionally unconverted HFP) travels through product pipe (5) to the first distillation column (6). In distillation column (6), hydrogen fluoride, which is recycled via bottoms line (2) to feed pipe (1), is separated from the mixture of HFC 227ea, hydrogen fluoride and unconverted HFP. The mixture of HFC 227ea, residual hydrogen fluoride and HFP is fed via tops line (7) from the distillation column (6) to the second distillation column (8). HFP is fed via feed line (9) to column (8). A stream comprising HFP and essentially all the hydrogen fluoride content of the stream entering distillation column (8) via line (7) is removed from the top of distillation column (8) via line (3) and the product stream HFC 227ea is removed from the bottom of column (8) via bottoms lead (10).

Preferably, as shown in Figure 2, a portion of the stream in pipe (3) is diverted in the liquid phase through pipe (11) to separator (12) in which a HFP-rich phase is separated from an hydrogen fluoride-rich phase. The HFP-rich liquid phase is fed via line (13) to feed line (9) to distillation column (8). The hydrogen fluoride-rich liquid phase from separator (12) is returned via line (14) to tops pipe (3) to feed line (1).

In Figures 3 and 4, feed pipe (21) leads to a reactor (22), which optionally contains a fluorination catalyst. Product pipe (23) from the reactor (22) is in fluid-flow communication with a distillation column (24), which is for example a packed column. Distillation column (24) is typically operated at a pressure of around 12 bars with a tops

temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (24) is provided with a bottoms pipe (25), a tops pipe (26), which is in fluid-flow communication with feed-pipe (21), and feed line (27) below the point at which product pipe (23) is attached to it.

5 In Figure 4, tops pipe (26) from distillation column (24) is provided with a line (28) which is in fluid flow communication with phase separator (29). Phase separator (29) is provided with both line (30) in fluid-flow communication with line (26) and line (31) in fluid-flow communication with feed line (27).

In operation, the reactor (22) is charged through feed pipe (21) with a feed
10 stream containing hydrogen fluoride (fresh and recycled through a hydrogen fluoride-rich stream (from line (26)) and recycled HFP. The product from separator (29) (HFC 227ea, hydrogen fluoride and optionally unconverted HFP) travels through product pipe (23) to distillation column (24). HFP is fed via feed line (27) to column (24). A stream comprising HFP and essentially all the hydrogen fluoride content of the
15 stream entering distillation column (24) via line (23) is removed from the top of distillation column (24) via line (26) and the product stream HFC 227ea is removed from the bottom of column (24) via bottoms lead (25).

Preferably, as shown in Figure 4, a portion of the stream in pipe (26) is diverted in the liquid phase through pipe (28) to separator (29) in which a HFP-rich phase is
20 separated from a hydrogen fluoride-rich phase. The HFP-rich phase from column (24) is fed via line (31) to feed line (27) to distillation column (24). The hydrogen fluoride-rich phase from separator (29) is returned via lines (30) and (26) to feed line (21).

In Figure 5, distillation column (32) is provided with feed line (31) connected to a reactor (not shown), feed line (33), bottom line (34) and top line (35). In operation, a
25 mixture comprising HFC 227ea/HF azeotrope, or azeotrope-like mixture, HFP/HF azeotrope, or azeotrope-like mixture and/or HF is fed via line (31) to distillation column (32) and a stream comprising HFP is fed via line (33) to distillation column (32). HFP/HF azeotrope, or azeotrope-like mixture, is removed from distillation column (32) via top line (35) and HFC 227ea substantially free from HF is removed from distillation
30 column (32) via bottom line (34).

The present invention is further illustrated by reference to the following Example.

Example

The Example reveals that both HFP and HFC 227ea form azeotropes with HF and, at constant pressure the boiling point of the HFP/HF azeotrope is lower than the boiling point of the HFC 227ea/HF azeotrope.

A temperature/composition plot for the HFC 227ea/HF binary is illustrated in Figure 6 wherein the dashed line ---- represents the vapour phase composition and the solid line represents the liquid phase composition. From Figure 6 it can be seen that at 174psi the HFC 227ea/HF azeotrope has a boiling point of 123°F and a composition of 42mole% HF and 58mole% HFC 227ea.

A temperature/composition plot for the HFP/HF binary is illustrated in Figure 7 wherein the dashed line ---- represents the vapour phase composition and the solid line represents the liquid phase composition. From Figure 7 it can be seen that at 174psi the HFP/HF azeotrope has a boiling point of 98°F and a composition of 38mole% HF and 62mole% HFP.

20

25

30

Claims

1. A process for the preparation of a fluorine-containing organic compound by reacting a haloalkene with hydrogen fluoride
wherein both the fluorine-containing organic compound and the haloalkene separately
5 form azeotropes, or azeotrope-like mixtures, with hydrogen fluoride and
wherein the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof,
is more volatile than the fluorine-containing organic compound/hydrogen fluoride
azeotrope, or azeotrope-like mixture thereof,
characterised by the Steps of:
- 10 A. charging the haloalkene and the mixture comprising the fluorine-containing
organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture and
optionally the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture and/or
hydrogen fluoride, arising from the reaction of the haloalkene with hydrogen fluoride to
a distillation column; and
- 15 B. recovering the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like
mixture, and the fluorine-containing organic compound from the distillation column
separately.
2. A process as claimed in Claim 1 further characterised by the step of separating at
least a portion of the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture,
20 recovered from Step B into a haloalkene-rich liquid phase and a hydrogen fluoride-rich
liquid phase.
3. A process for the preparation of a fluorine-containing organic compound by
reacting a haloalkene with hydrogen fluoride
wherein both the fluorine-containing organic compound and the haloalkene separately
25 form azeotropes, or azeotrope-like mixtures, with hydrogen fluoride and
wherein the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof,
is more volatile than the fluorine-containing organic compound/hydrogen fluoride
azeotrope, or azeotrope-like mixture thereof,
which comprises the step of :
- 30 A. charging a mixture comprising a haloalkene and hydrogen fluoride to a reactor;
and

- B. optionally recovering at least a portion of hydrogen fluoride from the reaction products from the reactor in Step A by distillation characterised by the further Steps of:
- C. charging the haloalkene and the mixture comprising the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, and HF from the reactor in Step A or, where Step B is carried out, the haloalkene and the mixture comprising the fluorine-containing organic compound/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, and the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, from Step B to a distillation column;
- D. recovering a haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, from the distillation column in Step C; and
- E. recovering the fluorine-containing organic compound substantially free from hydrogen fluoride from the distillation column in Step C.
4. A process as claimed in Claim 3 characterised by the further step of separating at least a portion of the haloalkene/hydrogen fluoride azeotrope, or azeotrope-like mixture thereof, recovered in Step D into a haloalkene-rich phase and a hydrogen fluoride-rich phase.
5. A process as claimed in Claim 1 or 3 wherein the fluorine-containing organic compound is a hydrofluorocarbon and the haloalkene is a fluoroalkene.
6. A process as claimed in Claim 5 wherein the hydrofluorocarbon is HFC 227ea and the fluoroalkene is HFP.
7. A process as claimed in Claim 3 wherein the haloalkene-rich phase from Step F is returned to the distillation column in Step C and the hydrogen fluoride-rich phase from Step F is recycled to the reactor in Step A.
8. An azeotrope, or azeotrope-like mixture, of HFC 227ea and hydrogen fluoride.
9. An azeotrope, or azeotrope-like mixture, of HFP and hydrogen fluoride.

Fig.1.

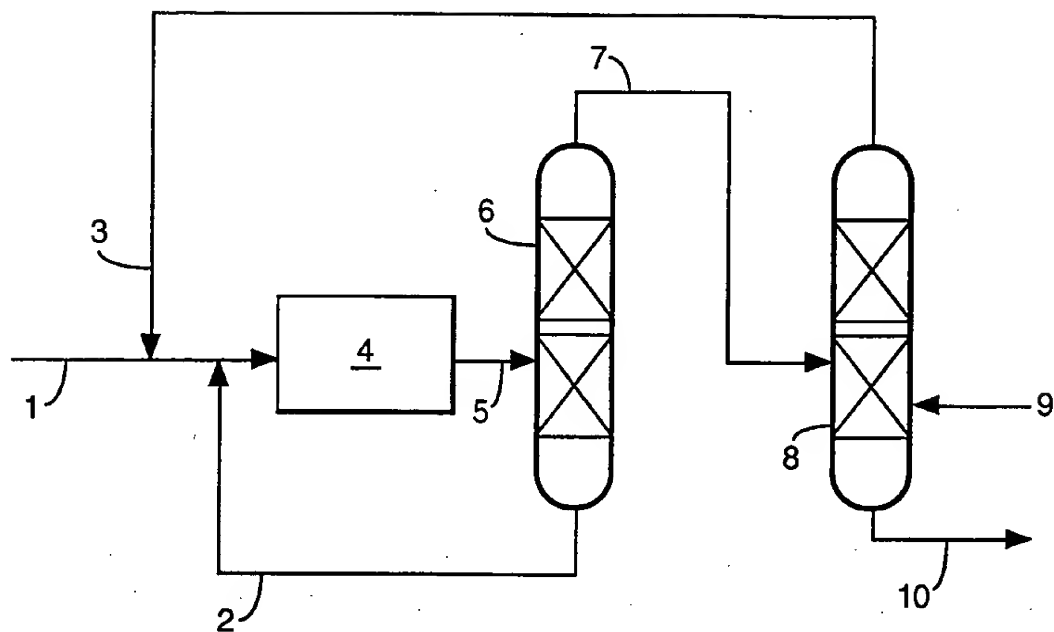
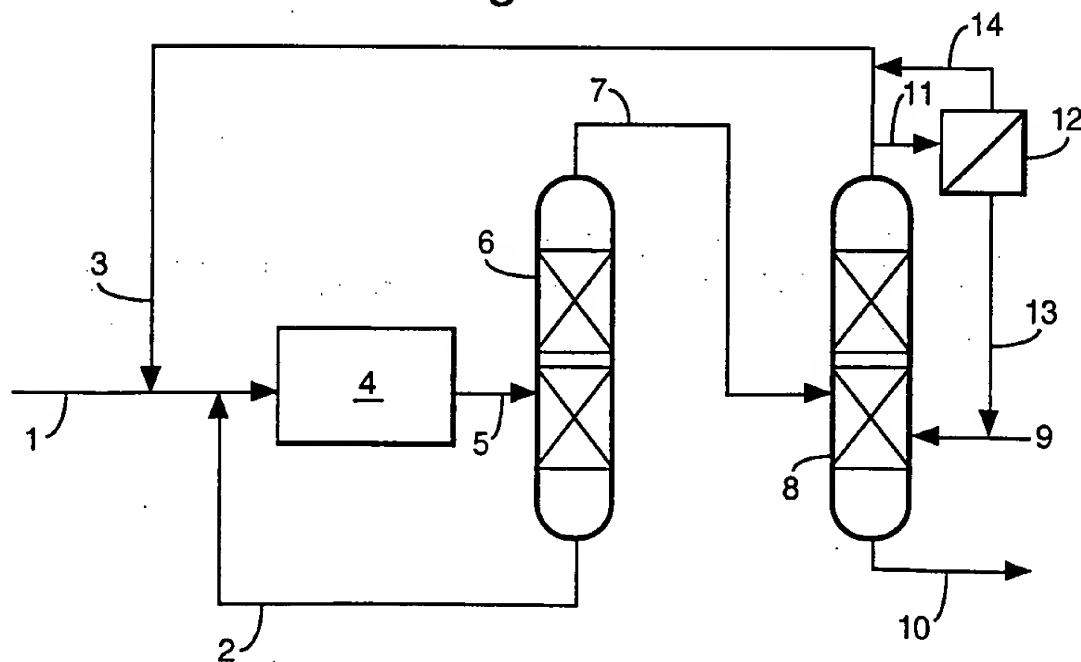


Fig.2.



2/4

Fig.3.

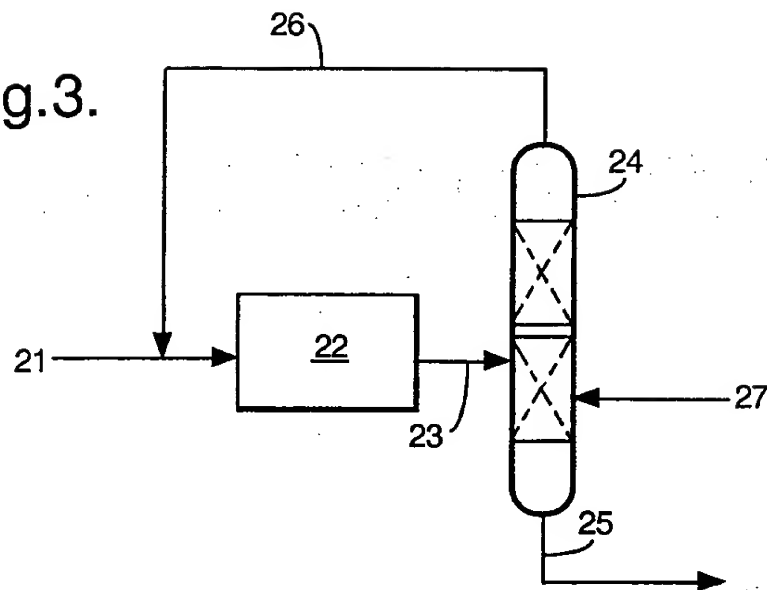


Fig.4.

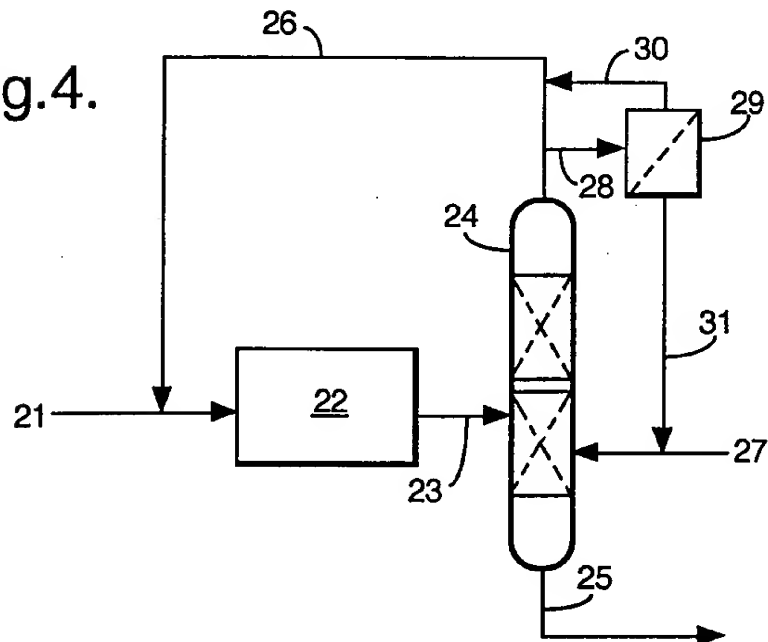
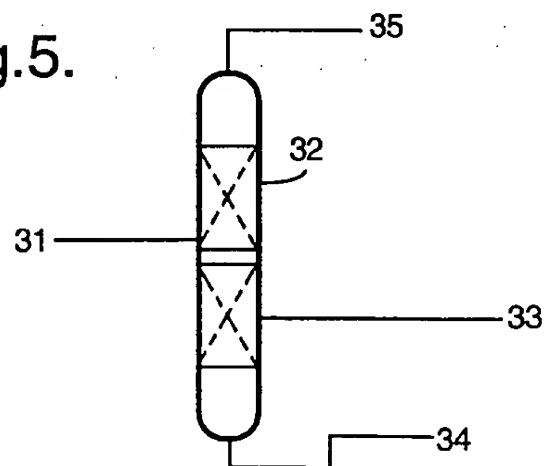


Fig.5.



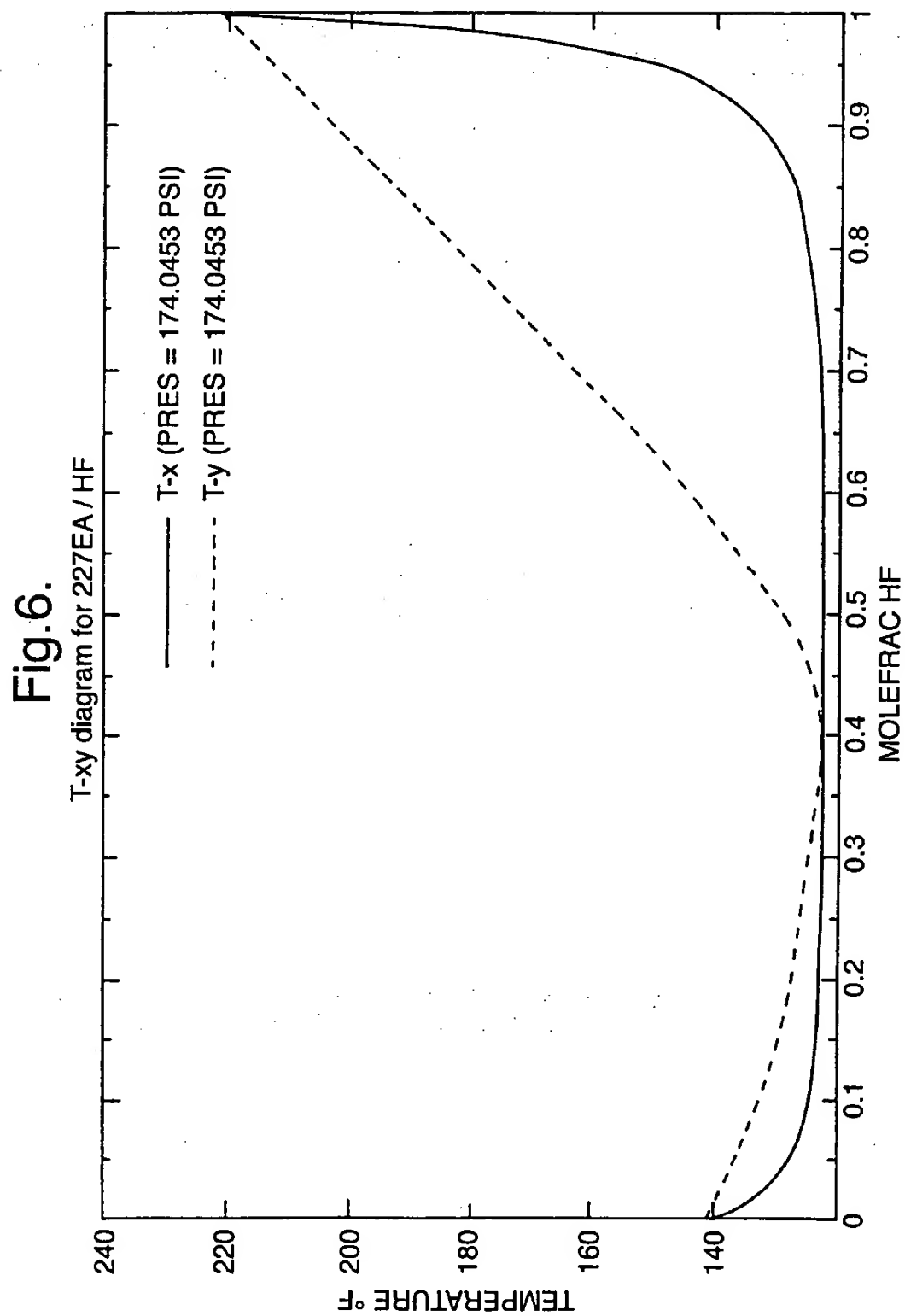
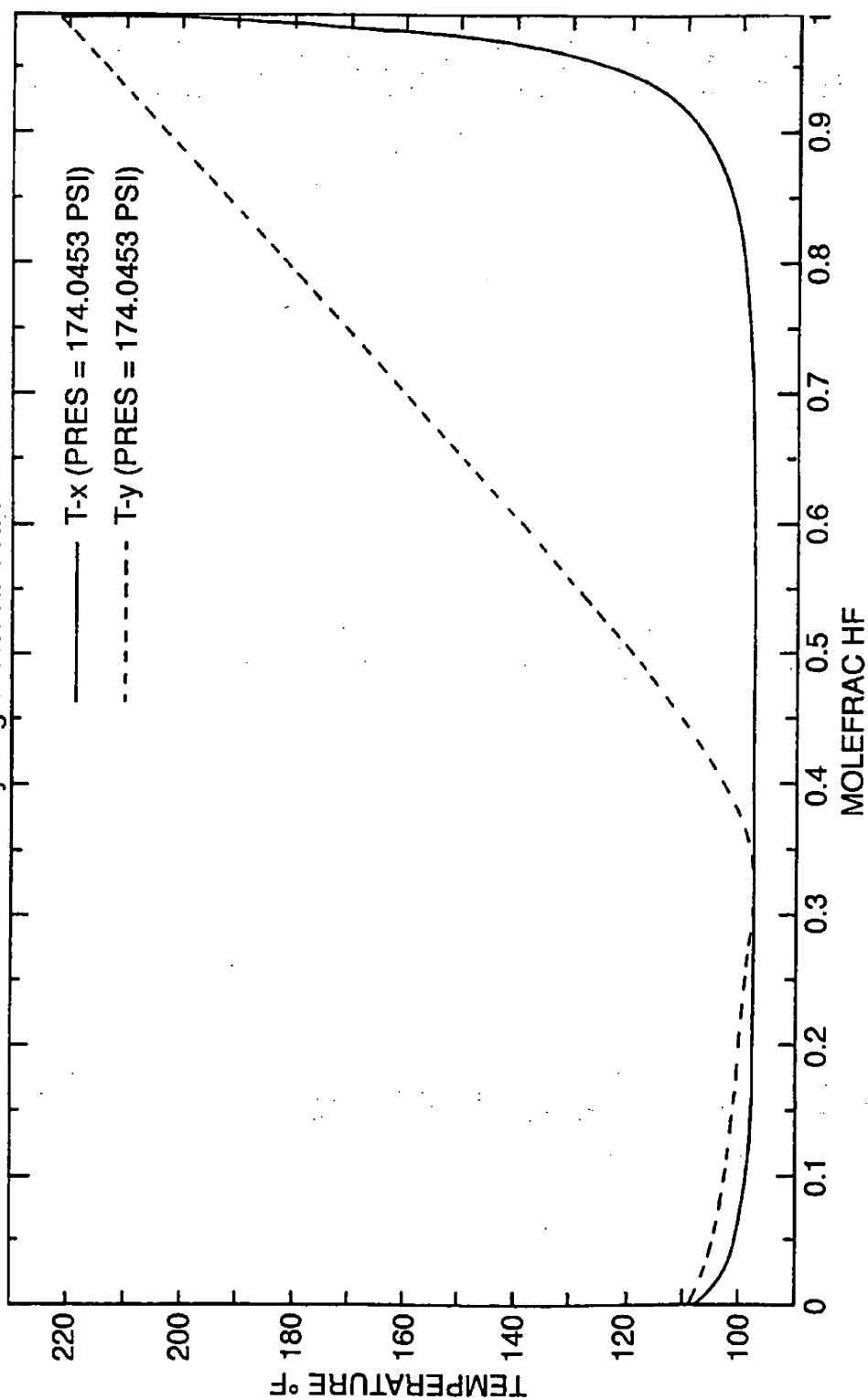


Fig.7.

T - xy diagram for HF / HFP



INTERNATIONAL SEARCH REPORT

National Application No

PCT/GB 98/03408

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/38 C07C19/08 C07C21/18 C07C17/386 C07C17/087

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 467 531 A (ICI PLC) 22 January 1992 see the whole document ---	1,3,5
A	US 5 475 169 A (HOPP PETER ET AL) 12 December 1995 see claims ---	1,5,6
A	GB 2 277 087 A (ICI PLC) 19 October 1994 see the whole document ---	1
A	WO 95 32935 A (DU PONT) 7 December 1995 see claims -----	8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 February 1999

Date of mailing of the international search report

15/02/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/03408

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0467531 A	22-01-1992	AU 631745 B	03-12-1992
		AU 7924291 A	09-01-1992
		CA 2045753 A	05-01-1992
		CN 1061587 A,B	03-06-1992
		DE 69104426 D	10-11-1994
		DE 69104426 T	16-02-1995
		DK 467531 T	31-10-1994
		ES 2062687 T	16-12-1994
		IE 65629 B	01-11-1995
		JP 2680945 B	19-11-1997
		JP 4261126 A	17-09-1992
		US 5211020 A	18-05-1993
US 5475169 A	12-12-1995	DE 4115025 A	12-11-1992
		AT 150744 T	15-04-1997
		CA 2068128 A	09-11-1992
		DE 59208257 D	30-04-1997
		DK 512502 T	22-09-1997
		EP 0512502 A	11-11-1992
		ES 2101768 T	16-07-1997
		GR 3023875 T	30-09-1997
		JP 5124999 A	21-05-1993
		SG 46681 A	20-02-1998
GB 2277087 A	19-10-1994	WO 9424077 A	27-10-1994
WO 9532935 A	07-12-1995	US 5563304 A	08-10-1996
		EP 0763004 A	19-03-1997
		JP 10500957 T	27-01-1998